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I. A STUDY IN THE PREPARATIONS
OF GLYCOLS

II. THE MECHANISMS OF THE
HYDROLYSIS OF AROMATIC AMINES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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A Study in the Preparation of Glycols.

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Part One

A Study in the Preparation of Glycols.

Introduction

When this investigation was begun, there was considerable interest in the preparation of glycols by newer and cheaper methods because of the possibility of using polyhydroxy alcohols other than glycerol, in the manufacture of explosives. The di-nitrate of ethylene glycol, which corresponds to nitroglycerin, is a very powerful explosive and the advantages of a cheap method of preparing glycol are readily apparent. It is obvious that the ordinary methods, such as boiling ethylene bromide with a solution of potassium carbonate, or heating ethylene bromide or chloride with sodium acetate and then saponifying the ester formed, are too expensive to be considered available for use in the manufacture of glycol in large quantities for the explosive industry. Moreover, any method involving the use of halogen was considered objectional because of the enormous demand for both chlorine and bromine in the manufacture of toxic products for gas warfare.

Cheap glycol could also be used as a substitute for glycerol in other minor instances; its use for the retention of moisture in tobacco and other commodities, its value in anti-freeze mixtures, and its use in medicine, may be mentioned as examples.

Theoretical Part.

Three methods of attacking this problem were considered. If carbon monoxide could be reduced with a suitable catalyst in such a manner as to cause a combination of two atoms of carbon, it might be possible to prepare glycol from carbon monoxide and hydrogen. These two products are cheap and barring expensive catalyzers, a cheap synthesis of glycol might be worked out. The work of Satatier (1) is interesting in this connection. He has shown that passing hydrocarbons and hydrogen through heated, metal tubes causes catalytic reduction to take place. The second method considered was that of the addition of two molecules of water to one molecule of acetylene by means of suitable catalyzers. The third method was the addition of hydrogen peroxide to ethylene, which would give glycol. These products are both more expensive than those in the other methods mentioned, but in view of the work of Fenton and Jackson (2) it seemed that this offered greater possibilities of success. Fenton and Jackson have shown that on oxidizing polyhydroxy alcohols, in the presence of ferrous sulphate, by means of hydrogen peroxide, the corresponding aldehydes are obtained. In the absence of the ferrous sulphate, no oxidation takes place. The ferrous salt undoubtedly has a catalytic effect.

Experimental Part

Oxidation of Allyl Alcohol by Hydrogen Peroxide: 10 cc. of ethyl alcohol were diluted with 30 cc. of water, warmed in the steam bath and 194 cc. of 3% hydrogen peroxide were added. On distilling, there was no high boiling portion, thus showing the absence of glycerol. This experiment was repeated, adding a small amount of ferric sulphate solution as a catalyzer. Again there was no oxidation. The use of an excess of hydrogen peroxide did not cause the reaction to take place.

Effect of Standing: A mixture of five cc. of allyl alcohol and 97 cc. of hydrogen peroxide were allowed to stand for several days. (solution A). At the same time a like mixture with ferric sulphate added was prepared and also allowed to stand (solution B). The amounts of hydrogen peroxide in these solutions were determined at frequent intervals. This was done by filling an eudiometer tube with KMnO_4 in acid solution and inserting it in a beaker containing some of the same solution. 1 cc. of the peroxide mixture was introduced at the bottom of the tube by means of a pipette, the end of which had been drawn into a capillary and curved back on itself in the shape of a small hook. By the oxidation of the peroxide oxygen is liberated and this allows the permanganate to fall in the tube giving un-reduced solution at the point where the peroxide is introduced. This gives a fairly accurate approx-

imation of the strength of the peroxide solution. The hydrogen peroxide content of solution A gradually decreased and in a week had become practically zero, while solution B showed almost no decrease. This indicated that there was either an actual oxidation of the alcohol or a decomposition of the peroxide. It was found that considerable less .1 N. potassium permanganate was required to oxidize 1 cc. of the solution A after standing than was required by 1 cc. of a mixture of the same amount of allyl alcohol and water. If the hydrogen peroxide had decomposed into water and oxygen without oxidizing the alcohol, the two solutions should have required the same quantity. This indicates that there must have been some oxidation of the alcohol. Evaporation of solution A left a dark, viscous residue, but on distilling this under diminished pressure the mass charred and no glycerol was obtained. Repeated attempts were made to identify glycerol by the preparation of the tribenzoate (3) but these failed.

Effect of Catalyzers upon the Oxidation of Allyl Alcohol:
Mixtures containing the same proportions as above were made up, using MnSO_4 and CuSO_4 as catalyzers. These solutions were allowed to stand and were tested at intervals for their peroxide content as previously described. Both the manganese and copper salts caused hardly a noticeable decrease in the amount of oxygen liberated by one cc. after standing five days, showing that the reaction or decomposition did not proceed as

rapidly in the presence of these salts as it did in the presence of ferric sulphate.

Mixtures of allyl alcohol, hydrogen peroxide and the different salts were refluxed one-half hour. At the end of that time there was a large decrease in the volume of oxygen liberated from 1 cc. of the solution. This was probably due to the decomposition of the peroxide on heating. A solution which was refluxed without the addition of a salt decomposed more slowly than those to which a salt had been added.

On evaporation of the refluxed mixtures, dark, viscous residues were obtained which did not yield glycerol on distillation under diminished pressure.

Attempt to Identify Glyceric Acid: It was found that there was an increased acidity in the mixtures after refluxing and it was thought that glycerol, if formed, might be oxidized to the corresponding acid. Attempts were made to show the presence of glyceric acid by preparation and purification of the lead salt. From this it was hoped to obtain the free acid and then to prepare B-iodopropionic acid by the action of P_2I_4 on the glyceric acid (4). The refluxed mixture was treated with an excess of $PbCO_3$ and allowed to stand for two days. At the end of this time, it still gave an acid reaction. It was then heated on the steam bath for several hours and filtered hot. The filtrate was concentrated and then cooled. A small amount of dark, dirty crystals, which could not be purified by recrystallization from hot water separated out. These



closely resembled some crystals obtained by a similar treatment of glyceric acid, but as the crystals from the refluxed mixtures could not be obtained pure, this attempt was abandoned.

Tests for Aldehydes in the Oxidation Product: Fenton and Jackson (2) have shown that the principal oxidation products of polyhydric alcohols are the corresponding aldehydes. Tests made with fuchsin aldehyde-reagent on the various mixtures obtained in the above attempts at oxidation were negative.

Attempts to Prepare Ethylene Glycol from Ethylene:

Ethylene was passed through a 3% hydrogen peroxide to which a small amount of ferric sulphate had been added. The solution was kept at 80-90° in a water bath. The peroxide merely decomposed. In another attempt alcohol and a trace of acetanilide were added, the first to hold the ethylene in solution and the second to stabilize the peroxide. These reagents performed their functions to some extent, but still there was no oxidation of the ethylene. A 13% hydrogen peroxide gave no better results.

Conclusions.

Altho it was impossible to obtain yields of a pure oxidation product, it seems that there is a reaction of some kind between the peroxide and the allyl alcohol for two reasons. First, less KMnO_4 is required to oxidize the mixture after refluxing than would be required if the peroxide merely decomposed into water and oxygen. Second, the acidity of the solute is increased after refluxing.

Work done in this laboratory recently by E. E. A. Campbell shows that in using hydrogen peroxide as an oxidizing agent, for organic compounds, very concentrated solutions, (50% or more,) should be used. In view of this and the results obtained above, it would seem that it may be possible to oxidize both allyl alcohol and ethylene to the corresponding glycols.

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- (2) Fenton and Jackson, J.O.C. 75, 1.
- (3) Mulliken "Identification of Pure Organic Compounds", Vol. I, Page 169.
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Part Two
The Mechanism of the Hydrolysis
of
Aromatic Amines
Introduction

It has been known for some time that p-nitroso dimethylaniline on heating with alkali, liberates dimethyl amine with the formation of p-nitrosophenol. Since aniline or dimethylaniline do not give analogous reactions, it is evident that the nitroso group has some effect in causing the hydrolysis to take place. Thus far there seems to have been no recorded attempt to explain and demonstrate the mechanism of this reaction. The object of this investigation, then, is to demonstrate an explanation for the above reaction.

Theoretical Part.

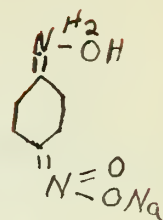
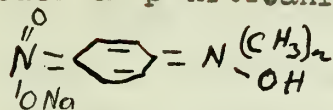
The hydrolysis of certain aromatic amines can be explained by assuming the formation of an intermediate addition product with alkali, $(CH_3)_2N= \underset{\text{OH}}{\text{C}}_6\text{H}_4 = N-ONa$, with a subsequent splitting off of the amine according to the usual behavior of compounds possessing a $=N-R$ linkage. The other products formed in this illustration is the sodium salt of p-nitroso phenol,



It will be seen that the

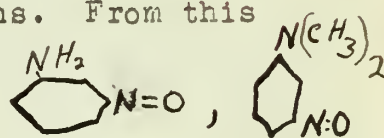
assumed intermediate product could also be formed in the

case of p-nitroaniline or its dimethyl derivative,



and that these compounds should also hydrolyze into the corresponding amine and p-nitrophenol. Furthermore, the intermediate compound contains the quinoid group, $= \text{C}_6\text{H}_4 =$, which

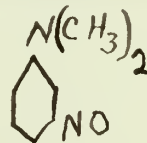
can exist only in ortho and para combinations. From this one would suppose that such compounds as



and the corresponding nitro-compounds would not hydrolyze.

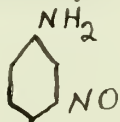
In order to investigate this explanation, it seems advisable to prepare compounds which should not hydrolyze and some which should in order to study their behavior toward alkali. Since p-nitroso-aniline derivatives are perhaps more commonly known as compounds which hydrolyze, interest naturally falls on the corresponding meta-compounds. The preparation of these compounds is one of the important problems in this investigation and much of the work consisted in attempts

to prepare m-nitrosodimethylaniline,



, and

m-nitrosoaniline,



. Two methods were attempted.

Gathermann (1) proposes as a general method for the preparation of aromatic nitroso compounds, the reduction of an aromatic nitro group to the corresponding hydroxylamine by zinc dust in neutral solution and the subsequent oxidation of the hydroxylamine group by means of chromic acid. Caro (2) proposes

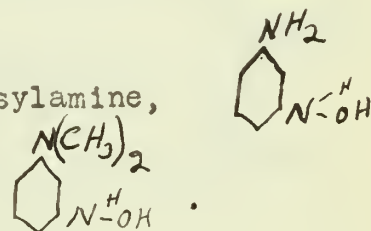
the oxidation of the NH_2 group to NO by "Caros acid" as a method of preparing aromatic nitroso compounds.

A study of the compounds which hydrolyze and those which do not, should give some indication of the correctness of the explanation.

Experimental Part.

Preparation of m-Nitrodimethylaniline: The m-nitro dimethyl aniline was prepared by mixing m-nitroaniline and dimethylsulphate in proportions of 1:2 by weight, the nitroaniline being added gradually to the sulphate at 150-160°. (3) When the reaction was complete, alkali was added and the mixture steam distilled. Instead of extracting with ether as desired by Ullmann, the distillate was first filtered and then extracted with benzene. This is more satisfactory as the benzene is more insoluble in water than ether and a more complete extraction is possible. The benzene was removed by distillation and the product which was filtered off before extraction was added to the residue. A sufficient amount of acetic anhydride to react with the nitro mono-methyl aniline was added and the mixture heated on the steam bath for about one-half hour. It was then cooled, diluted with hydrochloric acid, and extracted with ether to remove the acetyl derivative of m-nitro-monomethylaniline. The acid solution of m-nitrodimethylaniline was then made alkaline, the precipitate was filtered off and recrystallized from alcohol. The product formed beautiful red crystals, which melted at 61°.

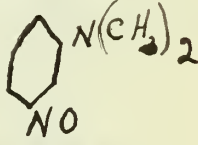
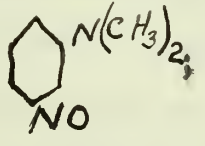
Attempts to Prepare m-Aminophenylhydrosylamine,
and m-Dimethylaminophenylhydroxylamine,



Method of Gathermann (5): Stirring m-nitrodimethylaniline or m-nitraniline with water,, calcium chloride, and zinc dust

at 15° gave a light brown oil which turned green before the reaction was complete and became sticky. It was not possible to obtain any pure product from the reaction mixture.

Preparation of m-Diaminoazobenzene: Several attempts to reproduce a German patent (4) by reducing m-nitraniline with zinc dust in 70% alcohol in the presence of calcium chloride were unsuccessful. m-Nitraniline was shaken vigorously with an excess of zinc dust in the presence of calcium chloride in 70% alcohol till the solution was colorless. (These solutions turned green and then black on standing). The reduced solution was then filtered from the excess of zinc directly into 10% sodium hydroxide. The precipitate which forms was filtered off after standing about five minutes and discarded as it contained only the zinc which was not dissolved by the alkali. The filtrate was then cooled with ice for several hours with frequent stirring and then filtered again. This precipitate was recrystallized twice from benzene and then it was found to melt at 145.5-146°C. Attempts to oxidize this compound with sodium dichromate were unsuccessful. It was found that the properties of this compound correspond with those of m-diaminoazobenzene.

Attempts to Prepare m-Nitrosodimethylaniline, 
from m-Aminodimethylaniline,  M-Nitrodimethylaniline was reduced with zinc and hydrochloric acid until the solution was colorless. The excess zinc was filtered off and

the filtrate made strongly alkaline and extracted with benzene. The benzene was evaporated and the residue distilled under diminished pressure. The boiling point was found to be 162-164° at 27 mm. This method is much more rapid and gives better yields than the ordinary reduction (5) by tin and hydrochloric acid and a precipitation of the tin by hydrogen sulphide. The para compound with a boiling point of 170-174° at 33 mm. was prepared by the same method.

Determination of the Oxidizing Value of Caro's Acid, Caro's Acid is monopersulphuric acid and it is prepared by mixing ammonium persulphate with concentrated sulphuric acid and allowing the mixture to stand in the cold. Experiments were carried out to determine the treatment required for maximum oxidizing power. Ammonium persulphate was mixed with varying amounts of concentrated sulphuric acid and allowed to stand at 0°C. Mixtures of the same proportions were also allowed to stand different lengths of time. The mixtures after standing, were diluted to a definite volume by adding ice and cold water. A fractional part was taken and added to a solution of an excess of potassium iodide in water and then neutralized with NH_3 or NaHCO_3 (5 grams) was added. This degree of alkalinity is recommended for iodometric titrations by Talbot. (6). The iodine liberated was titrated with standard sodium thiosulphate with starch paste as an indicator. It was found that ammonium

persulphate and sulphuric acid mixed in proportions of 1 gram to 1 cc. and allowed to stand for one hour at 0°, gave the best results. Ten grams of ammonium persulphate treated in this manner were equivalent to .37 grams of oxygen in oxidizing power.

Experiments with Caro's Acid: Nitroso benzene has previously been prepared with the use of Caro's Acid(5). The reagent was prepared as above and mixed with aniline suspended in water, the mixture being kept cold. After a few minutes, the solution was neutralized with sodium ammonium carbonate, the solution became green and the nitroso-benzene was extracted with ether.

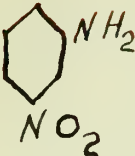

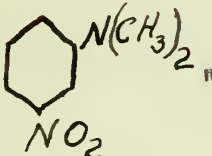
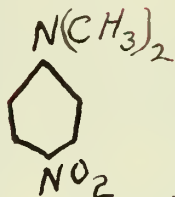
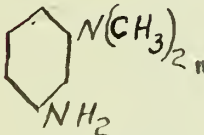
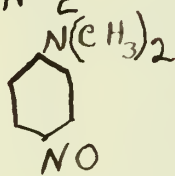
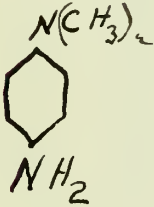
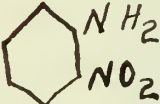
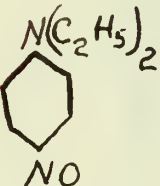
Attempts to prepare m-nitrosodimethylaniline by an analogous procedure gave different results in trials where conditions were apparently the same. In some cases a green solution would result on neutralization from which the green compound could not be extracted with ether or other solvents. In other attempts the solution would turn red or brown and at other times a gummy, sticky precipitate which could not be purified, would result. In view of these results it was considered best to investigate the hydrolysis of compounds which could be more readily obtained and to determine, if possible, the rates of hydrolysis.

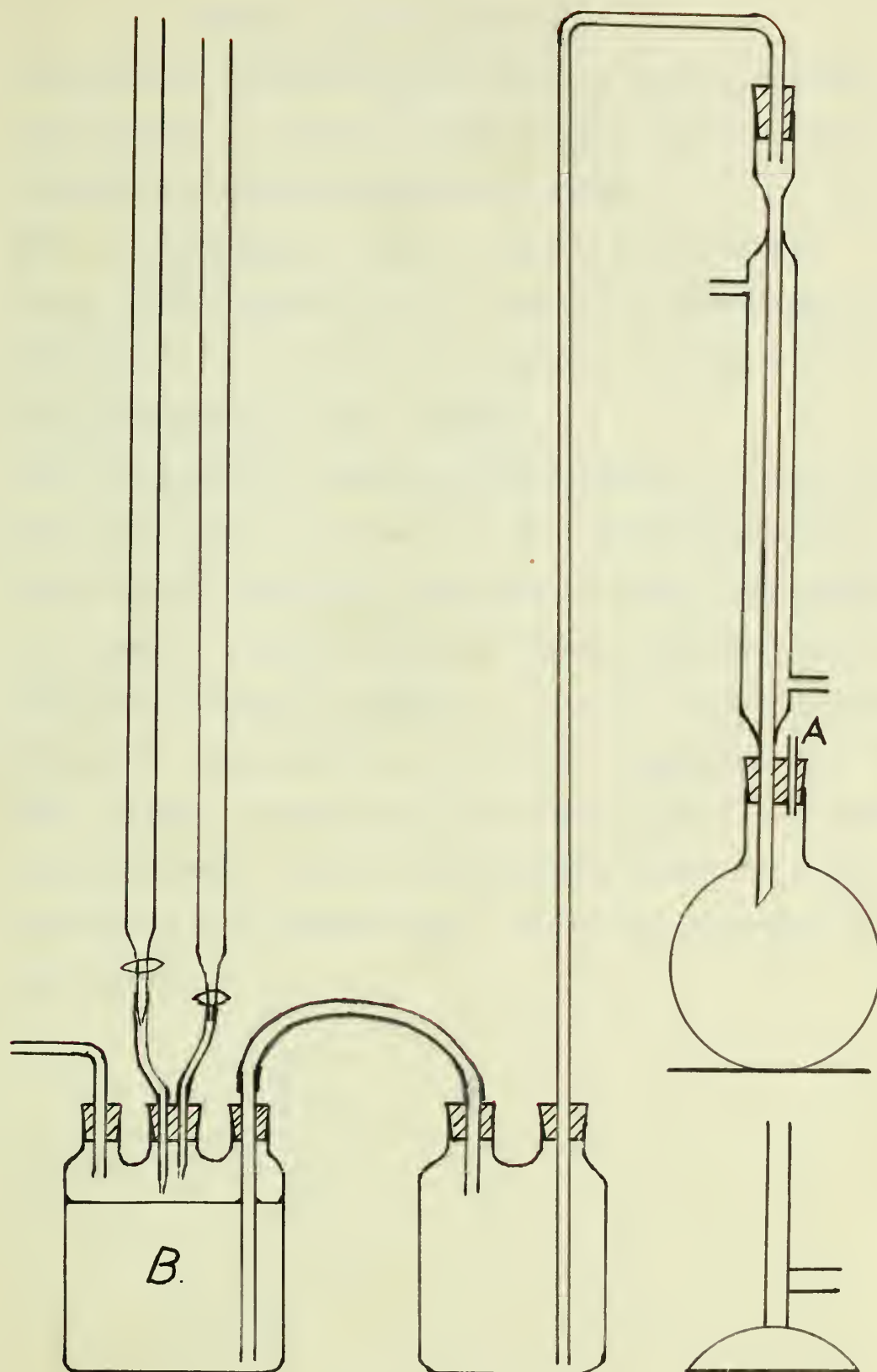
The Hydrolysis of Certain Amines.

The compounds shown in Table I were refluxed with 30% alkali to determine whether they would hydrolyze or not. Where

possible the rate of hydrolysis was measured by means of the apparatus illustrated in Fig. I. The amine is carried up through the reflux condenser and into the double-necked Wolff bottle which serves as a trap, from here it passes to the triple-necked bottle where it bubbles through the solution. One neck of the bottle contains a 2-hole rubber stopper, through which are passed the tips of two burettes. A current of air is continually passed through the apparatus by means of an air pump and a small tube through the stopper at A. The solution in the bottle B contains phenolphthaleium. 10 cc. of .5 N sulphuric acid were run in at a time and when this had been neutralized by the amine/^{or ammonia}as was shown by the indicator, the exact time and volume were read and from this data a curve showing the rate of hydrolysis was plotted. A fairly accurate comparison of the rates of hydrolysis was obtained for only two compounds, p-nitrosodimethylaniline and p-nitraniline. Of these the first hydrolyzed somewhat more readily than the second. The initial compounds are all slightly volatile and traces pass over into the solution and discolor it, making it difficult to see the end point. In many cases a measure of the rate of hydrolysis could not be obtained because the original material volatilized to such an extent that it completely hid the end point. From the results tabulated in Table I, it will be seen that the proposed explanation holds in every case.

Table I.

	Does not hydrolyze				Hydrolyzes
	"	"	"		"
	"	"	"		"
	"	"	"		"
					"



Summary and Conclusions.

1. m-Nitraniline reduced by zinc dust in neutral solution in the presence of Calcium chloride gives m-diaminoazobenzene instead of m-aminophenylhydroxyl amine.
2. The oxidizing value of Caro's acid was determined.
3. Altho nitroso benzene can be prepared by oxidation of aniline with Caro's acid, it was not possible to prepare m-nitroso-dimethylaniline by that method.
4. The fact that all compounds tested conform to the predictions which are made on the basis of the explanation of the mechanism of the hydrolysis, and also that many other compounds are known to conform with this theory, indicates that the mechanism proposed is correct. That is, an intermediate product of the quinone type is first formed and this breaks down, giving the amine and the sodium salt of the corresponding phenol. Since meta compounds cannot form addition products of the quinone type, they do not hydrolyze in this manner.

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